

# ION HYDRATION AND ION-PAIR FORMATION IN WATER

All salt species form contact ion pairs in a hydrothermal environment at temperatures near and above the critical point of water (375°C, 210 bar). In this report we present the first observation, using x-ray absorption spectroscopy, of the behavior of Cu ions and their surroundings in an environment where the hydrogen-bonded network of water has largely disintegrated, producing conditions wherein the local attractive forces between the negative and positive ions are greatly enhanced. Among many unexpected results, the formation of a stable linear dichloro  $\text{Cu}^{1+}$  species,  $(\text{CuCl}_2)^-$ , and an absence of hydrated water molecules in the first solvation shell of this dichloro species are most noteworthy.

Most mono- and divalent salts will fully dissociate in water to form separately hydrated negative and positive ions. The first shell of water molecules around these ions is very tightly bound, primarily through strong, local electrostatic forces. For some of the transition-metal salts, the dissociation is incomplete at high concentrations, and a fraction of the negative and positive ions remain associated in a structure known as a contact ion pair. However, *all* salt species form these contact ion pairs at temperatures near and above the critical point of water (375°C, 210 bar) where the electrostatic shielding properties of water have been diminished. In this hydrothermal environment, the hydrogen-bond network of water has largely disintegrated, producing conditions wherein the local attractive forces between the negative and positive ions are greatly enhanced. Until recently, little was known about the precise structure of these contact ion pairs, since probing their structure in near-critical water is experimentally challenging. X-ray absorption fine structure (XAFS) studies conducted at the PNC-CAT insertion device beamline (sector 20) have revealed fascinating details of these structures for the first time [1-3]. These results are rewriting the way we think about ions in water and thus will impact a large number of biological, geochemical, and industrial processes. Furthermore, these results

readily lend themselves to comparison with molecular dynamics, *ab initio*, and density functional methods because of the relatively simple structure and small size of the ion pairs.

For obtaining detailed structural information about the first hydration shell around ions, XAFS is an especially useful technique. With XAFS, one can focus on a particular type of atom or ion in the solution, thus excluding interferences from all other atoms. This aspect also allows one to look at very dilute solutions, since the disturbances from other atoms in the system are eliminated. Different regions of the XAFS spectra contain different types of chemical and structural information about the aqueous ions. The pre-edge and the x-ray absorption near-edge structure (XANES) regions, from about 20 eV below to about 30 eV above the absorption edge, contain information about the oxidation state and the coordination symmetry. The extended x-ray absorption fine structure (EXAFS) region, from 30 to about 1000 eV above the absorption edge, provides information about coordination numbers, bond distances, and bond disorder. Using the entire spectral range, a very detailed picture of the coordination structure can be obtained around the negative or positive ion or, in some cases, both species. Furthermore, coupling the XAFS analysis with molecular dynamics (MD) simulations has provided

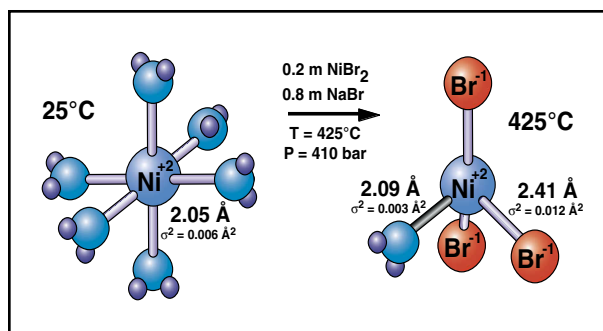


FIG. 1.  $\text{Ni}^{2+}$  coordination structure from the EXAFS, XANES, and pre-edge spectra.

an invaluable tool for clarifying certain aspects of the local ion structure. The MD simulations have also been used to determine whether or not the models that are currently used to predict the forces between ions and water and between the negative and the positive ion are realistic. This new and highly accurate approach to testing ion interactions has so far shown that we need significant improvements into our current set of models to accurately capture the behavior of ions in water under ambient and hydrothermal conditions.

The XAFS experiments were conducted in specially designed, high-pressure, high-temperature cells constructed from highly inert metal alloys. Small diamond windows are incorporated into the design to provide for the transmission of the focused, intense x-ray beam through the hydrothermal solutions. By adjusting the temperature of the solution in the range from 25 to 500°C at pressures up to 700 bar, the degree of ion-pair formation can be readily modulated.

The experimentally determined structures that have been derived from our XAFS measurements are shown schematically in Figs. 1 and 2. The room-temperature results confirmed previously known coordination structures about  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The details of the dramatic structural transition that occurs for the  $\text{Ni}^{2+}$  and  $\text{Cu}^{1+}$  high-temperature species have not previously been reported. For the  $\text{Ni}^{2+}$  ion at room temperature (Fig. 1), we found a rigid octahedral hydration structure with six water molecules bound at a distance of 2.05 Å (Ni-O). For  $\text{Cu}^{2+}$  (Fig. 2), there is a distorted octahedral structure where the two axial waters are at slightly clon-

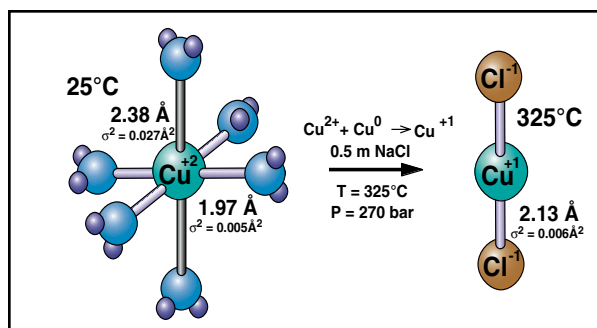
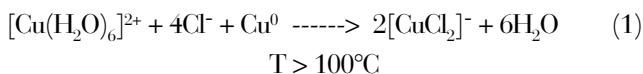


FIG. 2.  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  coordination structure from the EXAFS, XANES, and pre-edge spectra.

gated distances. In the XAFS analysis, the Debye-Waller factor,  $\sigma^2$ , is a measure of the mean square displacement of the bond distance due to thermal and structural disorder. Indeed, the very small value of  $\sigma^2$  for the room-temperature Ni-O distance means that the strength of this interaction is starting to approach the rigidity of a covalent bond. At 425°C, the first-shell symmetry changes from octahedral to tetrahedral as a contact ion pair forms that has on average about three  $\text{Br}^-$  ions and one  $\text{H}_2\text{O}$  molecule bound to the  $\text{Ni}^{2+}$  ion.

The high-temperature chemistry of Cu is somewhat more complex. First of all,  $\text{Cu}^{2+}$  is a rather strong oxidizer at elevated temperatures; thus,  $\text{Cu}^{1+}$  species are usually thermodynamically favored under hydrothermal conditions. Therefore, we introduced in our experiments an excess of  $\text{Cu}^0$  to the  $\text{Cu}^{2+}$  solution so that the  $\text{Cu}^{1+}$  could be studied under high-temperature conditions. We observed that the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  occurs immediately at temperatures near and above 100°C according to the reaction,



Using XAFS, the  $\text{Cl}^-$  coordination structure about  $\text{Cu}^{1+}$  in water was determined at temperatures up to 325°C. We discovered that a linear dichloro  $\text{Cu}^{1+}$  species,  $[\text{CuCl}_2]^-$ , is especially stable, being predominant from 100 to 325°C in the presence of excess  $\text{Cl}^-$ . Surprisingly, there is no evidence of hydrated water molecules in the first solvation shell of this dichloro species. One possible explanation for a lack of tightly bound water molecules is that the

Cu-Cl interaction may be partially covalent in nature. For all ions at high temperatures, entropic changes strongly favor the lowest coordination structures. In addition, when the ion pairs form, both the positive and negative ion lose all or most of their bound water in the first shell. This type of transition is also strongly favored entropically at higher temperatures. The other dominant factor driving ion-pair formation is the activation of the electrostatic attractions as the charge-screening property of water diminishes with the breaking of hydrogen bonds.

In summary, key insights into the structure and the speciation of electrolytes in high-temperature aqueous solutions are now being derived from XAFS spectroscopy. The future application of this technique to a range of chemically diverse ionic solutions will tremendously expand our understanding of these systems.

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